

Partial Translation of JP-A-04-154829\*

(Claims)

1. A curable composition comprising

5 (A) 100 parts by weight of a polymer having both a urethane linkage and a hydrolyzable silicon group, produced by a reaction of

(1) a polyether having a molecular chain end that is blocked with a hydroxyl group,

10 (2) a compound having two isocyanato groups in the molecule and

(3) an organosilicon compound having at least one selected from the group consisting of a isocyanato group and a group reactive with an isocyanato group, said  
15 isocyanato group or said group reactive with an isocyanato group being not directly bound to a silicon atom, and

said organosilicon compound also having a hydrolyzable group that is directly bound to the silicon atom,

20 (B) at least 2.5 and less than 100 parts by weight of a total amount of

(1) a compound having at least two epoxy groups in the molecule and

(2) an epoxy curing agent, and

25 (C) 0.01 to 30 parts by weight of a catalyst to promote hydrolysis of the hydrolyzable group bound to the silicon atom.

(Page 5, upper left column, lines 2 to 20)

30 The catalyst (C) to promote hydrolysis of the hydrolyzable silyl group is a component for rapidly hydrolyzing the hydrolysable silicon group which is present at the molecular chain end of the polymer of (A) to form a three-dimensional network structure. Examples of the  
35 catalyst (C) include tin carboxylates such as tin octylate;

organic tin carboxylates such as dibutyltin dilaurate, dibutyltin dimaleate, and dibutyltin phthalate; organic tin oxides and reaction products thereof with esters; organic titanates such as tetrabutyl titanate; amines; amine salts; quaternary ammonium salts; and guanidine compounds. The component (C) is preferably used in an amount of 0.01 to 30 parts by weight per 100 parts by weight of the polymer (A). If the amount of the component (C) is less than 0.01 parts by weight, it is not preferable because the curing rate of the polymer (A) becomes too slow to delay providing a cured substance with sufficient strength. On the contrary, if the amount of the component (C) is more than 30 parts by weight, it is not preferable since seepage or precipitation occurs after curing.

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(Examples)

Hereafter, the present invention will be described by Examples. As used herein, "part(s)" and "%" mean "part(s) by weight" and "% by weight", respectively.

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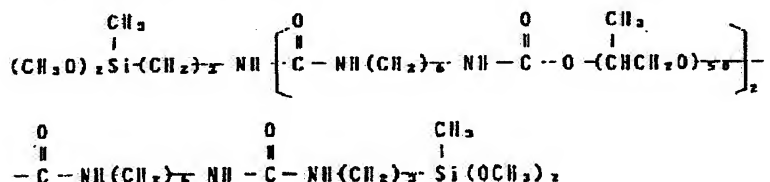
#### Synthesis Example 1

To 2 moles of polyether having a molecular chain end that is blocked with a hydroxyl group, which has a mean polymerization degree of 50, an average molecular weight of 3000, viscosity of 500 cSt at 25°C and a hydroxyl value of 37 mgKOH/g, 3 moles of hexamethylene diisocyanate, dibutyltin dilaurate in an amount of 0.1% of the total amount of the polyether and the hexamethylene diisocyanate, and glacial acetic acid were added, and the resulting mixture was stirred with heating at 60°C for 5 hours under

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a nitrogen atmosphere. Then, 2.2 moles of 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{N}(\text{CH}_2)_6\text{Si}(\text{OCH}_3)_2 \end{array}$$
 was added and the resulting mixture was further stirred for 2 hours under the same conditions to give a polymer

- (hereafter, referred to as "P-1") having a urethane linkage and a molecular chain end that is blocked with a hydrolysable silicon group, as a clear, colorless viscous liquid. The polymer had a typical structural formula represented by the following formula:



The polymer had viscosity of 74000 cSt at 25°C and a number average molecular weight of 7600 measured by GPC.

#### 10 Synthesis Example 2

- To 3 moles of polyether having a molecular chain end blocked with a hydroxyl group, which has a mean polymerization degree of 32, an average molecular weight of 2000, viscosity of 320 cSt at 25°C and a hydroxyl value of 57 mgKOH/g, 4 moles of a mixture of 2,4-trilene diisocyanate and 2,6-trilene diisocyanate, dibutyltin dilaurate in an amount of 0.1% of the total amount of the polyether and the mixture of diisocyanate, and glacial acetic acid were added, and the resulting mixture was stirred with heating at 60°C for 5 hours under a nitrogen

- atmosphere. Then, 2.2 moles of  $\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{NH}-(\text{CH}_2)_2-\text{Si}(\text{OCH}_3)_2 \end{array}$  was added and the resulting mixture was further stirred for 3 hours under the same conditions to give a polymer (hereafter, referred to as "P-2") having a urethane linkage and a molecular chain end that is blocked with a hydrolysable silicon group, as a clear, colorless viscous liquid. The polymer had a typical structural formula represented by the following formula:

## 5 Synthesis Example 3

$\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_2)_3$  was added and the resulting mixture was

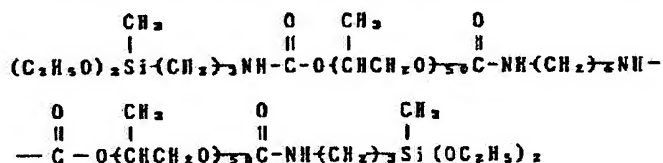
$$\begin{array}{c} \text{CH}_3 \\ | \\ (\text{CH}_2\text{O})_x \text{Si}-(\text{CH}_2)_y \text{S} \left\{ \begin{array}{c} \text{O} \\ || \\ \text{C}-\text{NH}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}-\text{C} \\ \text{O} \end{array} \right. \\ \\ \text{CH}_2 \\ | \\ -\text{O}-(\text{CHCH}_2\text{O})_z \left\{ \begin{array}{c} \text{O} \\ || \\ \text{C}-\text{NH}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}-\text{C} \\ \text{O} \end{array} \right. \text{S}- \end{array}$$

The polymer had viscosity of 58000 cSt at 25°C and a number average molecular weight of 6900 measured by GPC.

#### Synthesis Example 4

To 2 moles of the same polyether as in Synthesis Example 1, 1 mole of hexamethylene diisocyanate, dibutyltin dilaurate in an amount of 0.1% of the total amount of the polyether and the hexamethylene diisocyanate, and glacial acetic acid were added, and the resulting mixture was stirred with heating at 60°C for 3 hours under a nitrogen

atmosphere. Then, 2 moles of  $\text{OCH}-(\text{CH}_2)_3-\overset{\text{CH}_3}{\underset{|}{\text{Si}}}(\text{OC}_2\text{H}_5)_2$  was added and the resulting mixture was further stirred for 3 hours under the same conditions to give a polymer (hereafter, referred to as "P-4") having a urethane linkage and a molecular chain end blocked with a hydrolysable silicon group, as a clear, colorless viscous liquid. The polymer had a typical structural formula represented by the following formula:



The polymer had viscosity of 65000 cSt at 25°C and a number average molecular weight of 7200 measured by GPC.

#### Reference Example 1

Polyoxypropylene having a group:

$(\text{CH}_3\text{O})_2\text{Si}-\overset{\text{CH}_3}{\underset{|}{\text{CH}_2\text{CH}_2\text{CH}_2}}-\text{O}-$  at the molecular chain end, with an average molecular weight of 8000, is hereafter referred to as "P-5".

#### Examples 1 to 4 and Comparative Examples 1 to 3

To 100 parts of each of polymers P-1 to P-5 prepared in Synthesis Examples 1 to 4 and Reference Example 1, an

epoxy compound, an epoxy curing agent and a hydrolysis catalyst, which are shown in Table 1, were added, and each resulting mixture was mixed with a spatula to prepare samples 1 to 7. A sample was mixed again for 10 minutes with a spatula just after the first mixing. Another sample was mixed again at the time of any of 10, 30 or 60 minutes later from the first mixing. Then, each sample was spread out over a Teflon plate so that the thickness of the sample became about 2 mm and left to stand at 20°C with a relative humidity of 50%. A period from the time when the sample had been spread out over the Teflon plate to the time when the spread sample became dust-free (such a period is referred to as "tack-free time") was measured. Then, the sample was cured over the Teflon plate for 7 days under the same conditions, peeled off the Teflon plate, and punched out in a JIS No. 2 dumbbell shape. The properties of the dumbbell-shaped sample were tested. These results are also shown in Table 1.

Comparative Example 1 is a comparative example in which polyoxypropylene having a hydrolysable silicon group at a molecular chain end was used in place of the polymer (A) for the present invention. Comparative Example 2 is a comparative example in which the total amount of the epoxy resin and the epoxy curing agent exceeded that of the polymer (A) for the present invention. Comparative Example 3 is a comparative example in which the total amount of the epoxy resin and the epoxy curing agent exceeded that of the same polyoxypropylene having a hydrolysable silicon group at a molecular chain end as in Comparative Example 1.

TABLE 1

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3
Sample no.		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Polymer no.		P-1	P-2	P-3	P-4	P-5	P-4	P-5
Epoxy compound	Bisphenol A diglycidyl ether (Epoxy equivalent: 200)	80 parts	-	-	50 parts	50 parts	110 parts	110 parts
	Hydrogenated bisphenol A diglycidyl ether (Epoxy equivalent: 240)	-	70 parts	-	-	-	-	-
	Bisphenol F diglycidyl ether (Epoxy equivalent: 180)	-	-	70 parts	-	-	-	-
	Triethylenetetramine	5 parts	-	-	-	-	-	-
Epoxy curing agent	m-Xylenediamine	-	7 parts	-	-	-	-	-
	Isophorondiamine	-	-	7 parts	-	-	-	-
	ADEKA HARDENER EH-230 <Aliphatic polyamine produced by ADEKA Corp.>	-	-	-	15 parts	15 parts	30 parts	30 parts
Hydrolysis catalyst	Dibutyltin dilaurate	2 parts	2 parts	2 parts	-	-	-	-
	Reaction product of dibutyltin oxide/dioctyl phthalate = 1/1	-	-	-	1 part	1 part	1 part	1 part
Just after first mixing	Tack-free time, min	180	180	180	150	150	240	240
	Tensile strength, kgf/cm <sup>2</sup>	92	101	103	96	22	125	90
	Elongation, %	220	160	160	190	270	80	60
10 minutes later	Tack-free time, min	180	180	180	150	150	180	180
	Tensile strength, kgf/cm <sup>2</sup>	96	94	105	104	25	130	85
	Elongation, %	230	190	170	200	280	50	50
30 minutes later	Tack-free time, min	150	150	150	130	130	60	60
	Tensile strength, kgf/cm <sup>2</sup>	95	92	95	91	22	230	160
	Elongation, %	210	180	150	160	250	5	2
60 minutes later	Tack-free time, min	150	150	150	120	120	30	30
	Tensile strength, kgf/cm <sup>2</sup>	92	95	100	97	20	210	140
	Elongation, %	200	160	180	190	270	2	2